ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201500555

The Influence of Water on the Optical Properties of Single-Layer Molybdenum Disulfide

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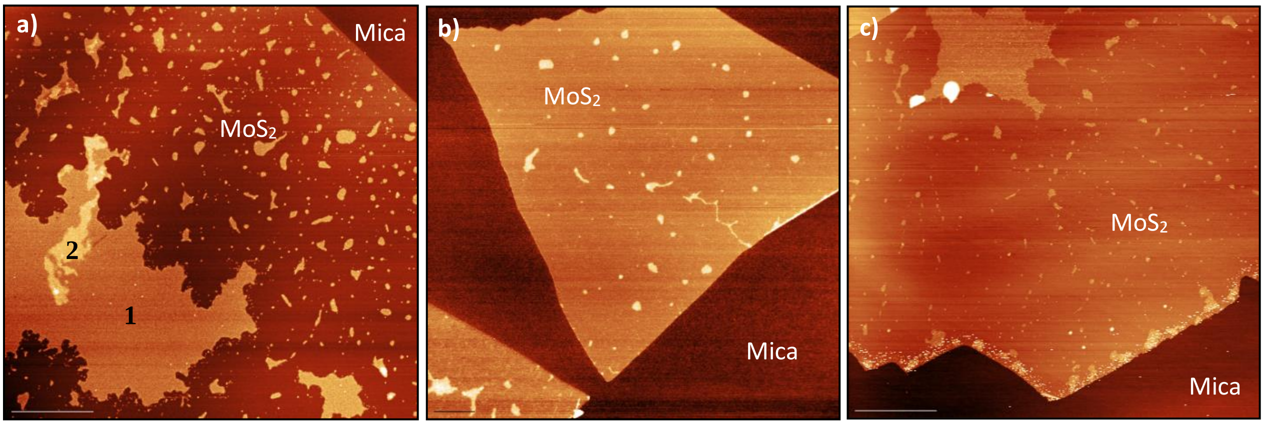

Figure S1 - Humidity Panel. a) AFM topograph of single-layer MoS_2 prepared at room temperature and relative humidity (RH) of 42%. Greater numbers of stacked adlayers are stabilized at higher humidities – 1 and 2 indicate first and second sets of ice layers respectively, where sets refer to multiple stacked ice adlayers. Adlayers would sometimes display mobility, changing shape over time when probed by the AFM tip. **b)** AFM topograph of single-layer MoS_2 prepared at room temperature and relative humidity of 5%. As can be seen in the figure, the size and frequency of water adlayers can be greatly reduced by lowering the relative humidity. The water layers become sporadic and appear as dot-like features. **c)** AFM topograph of a larger single-layer MoS_2 sample prepared at room temperature and relative humidity of 5%. Although mostly water-free with sporadic water structures, a larger water layer can be observed. Water could never be completely eliminated for any of our samples (larger layers could still be occasionally found at low humidities, though with less frequency). We consistently found exfoliation of molybdenum disulfide on the mica surface to be much more easily achieved at low relative humidity, with far greater yields of few-layer samples. Lateral scale-bar: a) 1 µm, b) 200 nm, c) 2 µm. Z-scale: a) 4 nm, b) 2 nm, c) 5 nm.

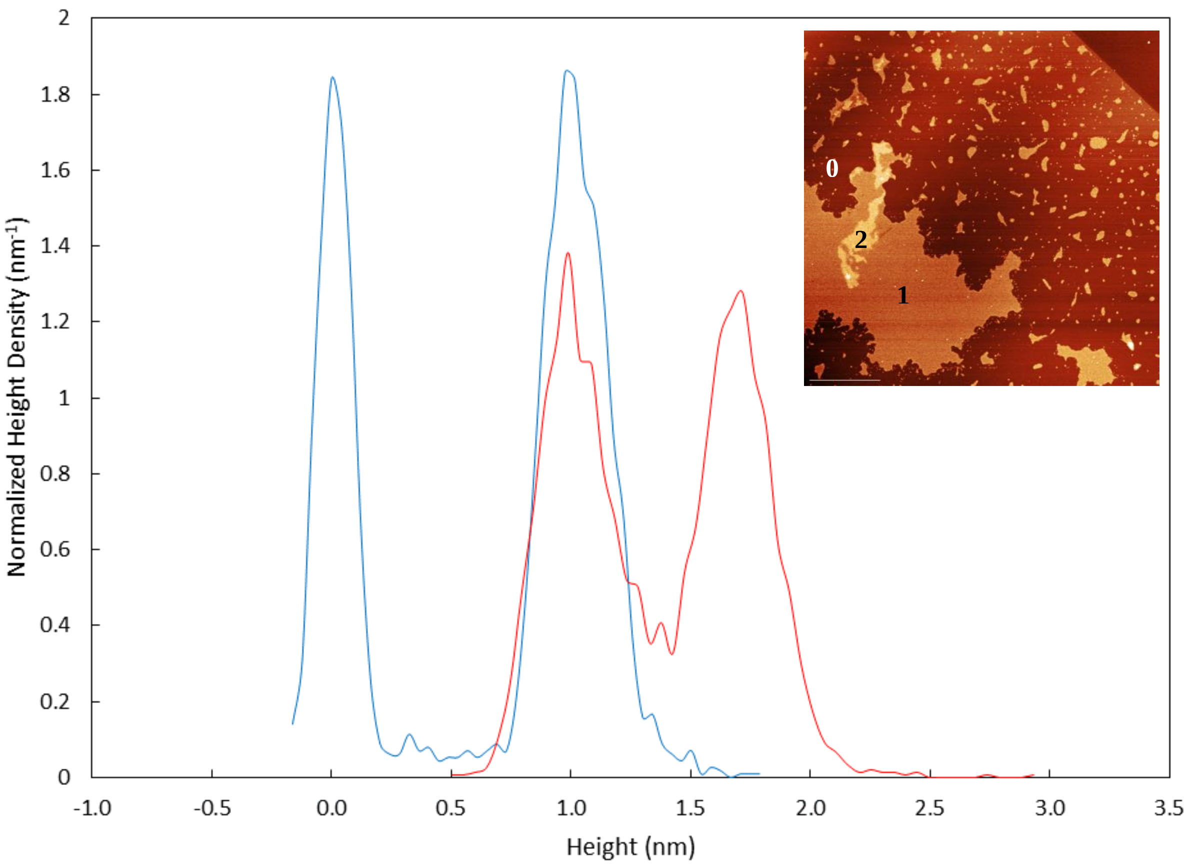

Figure S2 - Height histogram of Water Adlayers underneath Single-Layer MoS_2. For sample depicted in Figure S1a (shown in inset), individually normalized height density distributions are plotted in blue for no adlayers and first set of adlayers (corresponding to 0 and 1 in inset), and in red for first set of adlayers and second set of adlayers (corresponding to 1 and 2 in inset). Histograms were obtained from two images with a sampling window of 500 nm x 500 nm each. Distributions were overlaid to match the peak-centers of the first set of adlayers (at approximately 1 nm). The sharp peak features indicate the uniformity of the layers of ice observed underneath the MoS_2 flake. Lateral scale-bar: inset) 1 µm. Z-scale: inset) 4 nm.

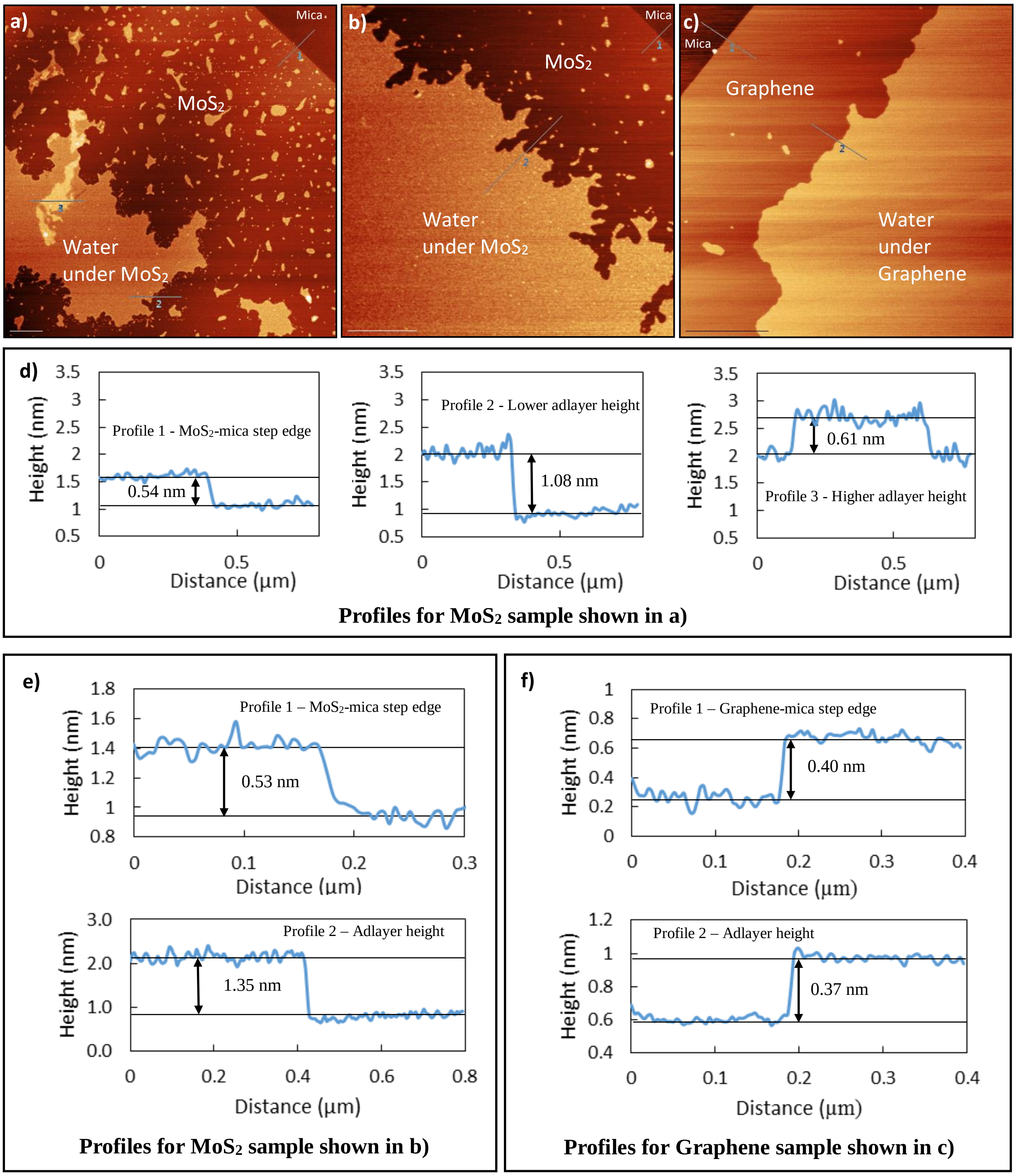

Figure S3 - Water Adlayers underneath Single-Layer MoS_2. a) AFM topograph of single-layer MoS_2 sample shown in Figure S1a reproduced above with blue lines indicating where profiles were taken for height analysis. (Sample prepared at 42% RH, room temperature). **b)** AFM topograph of another single-layer MoS_2 sample – shown in Figure 1b – reproduced above with blue lines indicating where profiles were taken for height analysis. (Sample prepared at 42% RH, room temperature). **c)** AFM topograph of single-layer graphene-templated mica sample acquired with same tip and at ambient conditions as for b). (Sample prepared at 52% RH, room temperature). Blue lines indicate where profiles were taken for height analysis. **d)** Height profiles for a) plotted in three separate graphs, taken along 1) MoS_2-mica step edge, 2) first water layer, 3) second water layer. **e)** Height profiles for b), taken along 1) MoS_2-mica step edge, 2) water layer. **f)** Height profiles for c), taken along 1) graphene-mica step edge, 2) water layer. Results for d, e, and f are summarized in table below. Values should be regarded as approximate, as measured heights can vary based on tip-sample interactions. Lateral scale-bar: a, b, c) 500 nm. Z-scale: a) 4 nm, b) 4 nm, c) 1.5 nm.

	Single-layer MoS_2	Single-layer Graphene
Step edge height from mica to single-layer material	0.53 nm, 0.54 nm	0.40 nm
Water layer height	1.08 nm, 1.35 nm, 0.61 nm (second layer)	0.37 nm

The theoretical thickness of a MoS_2 single-layer is 0.615 nm,[1] with reported measured heights including values ranging from 0.8-1 nm on SiO_2 (exfoliated),[2] 0.5-0.7 nm on bulk crystal MoS_2,[2] and about 0.7 nm on mica (epitaxial growth).[3] Our measured values for the thickness of exfoliated single-layer MoS_2 on mica are consistent with both theoretical and previously reported values. Measured values of the water layer heights indicate that single-layer MoS_2 stabilizes more water layers than graphene does.

The thickness of a graphene single-layer is 0.34 nm, with reported measured heights ranging from 0.4-0.9 nm on mica, and water layer heights ranging from 0.35-0.39 nm on the mica surface.[4] Our measured values are consistent with previously reported values for graphene-templating.

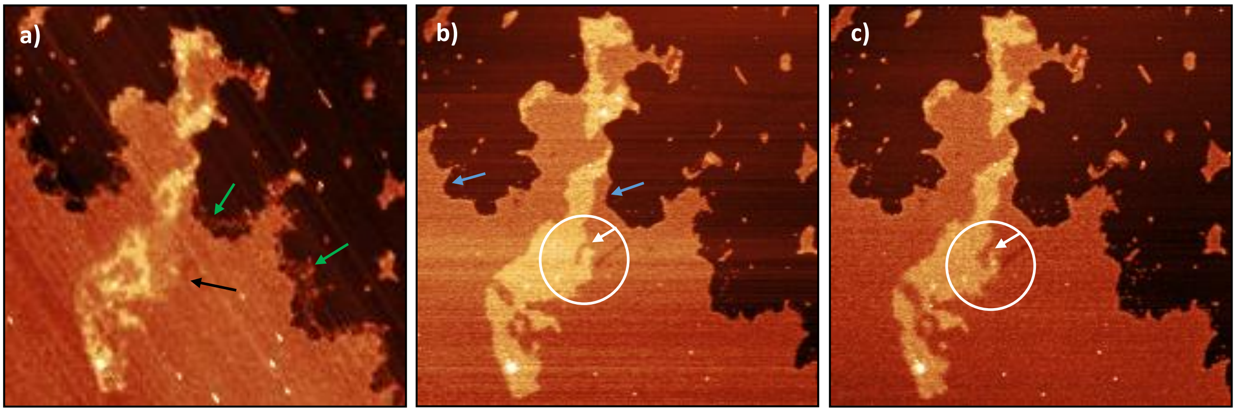

Figure S4 - Mobile Adlayers underneath Single-Layer MoS_2 on Mica. a) AFM topograph of single-layer MoS_2 on mica, revealing distinct water layers (image taken at earlier time of same sample shown in Figure S3a, rotated and cropped for comparison with images b) and c) that were acquired later at a different scan angle). Stacked adlayer appears to be forming (black arrow). Examining the lower adlayer reveals that the edges are still forming (green arrows). **b)** AFM topograph of same area in a) taken after scanning other areas and returning to same area, approximately 6 h later. A distinct water layer appears to have formed on top of the existing layer underneath. Blue arrows point to angles of about 120° between adlayer edges. **c)** Same area as b) after continuous scanning. Approximately 150 min later, adlayers still display subtle changes – for example, feature inside white circles marked in b) and c) displays change in shape over time. All topographs represent approximately the same 2 µm x 2 µm area. Z-scale: a) 3 nm, b, c) 4 nm.

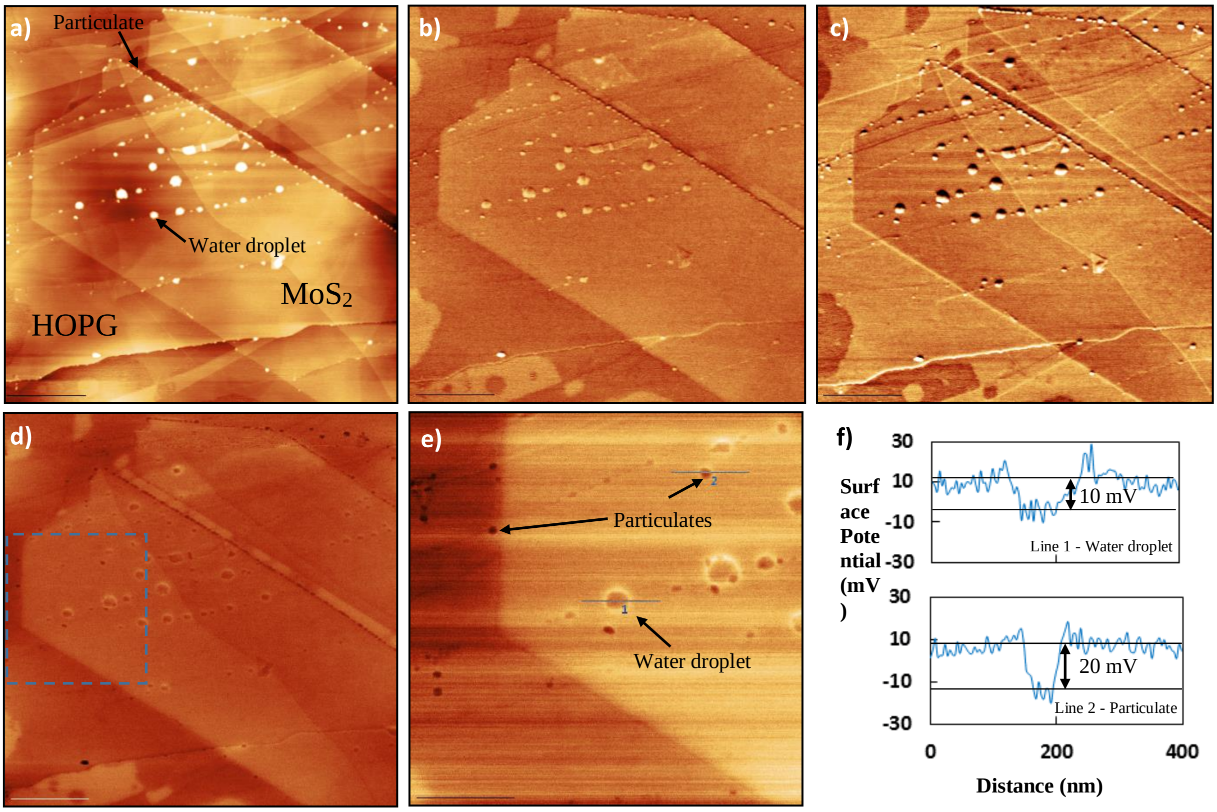

Figure S5 - Scanning Probe Images of Single-Layer MoS_2 on HOPG. a) AFM topograph of single-layer MoS_2 exfoliated on HOPG (42% RH and room temperature). Arrows point to particulate and water droplet. **b)** EFM image of same area shown in a) taken at 4 Volts. **c)** EFM image of same area taken at -4 Volts. **d)** KPFM image of same area. **e)** KPFM image taken of area indicated by blue square in d). Arrows point to water droplet trapped underneath single-layer MoS_2, as well as particulates on top of both HOPG and single-layer MoS_2. Particulates were often moved by the AFM tip on the surface. **f)** Surface potential profiles taken along blue lines labeled 1 (water droplet) and 2 (particulate) in e). Lateral scale-bar: a, b, c, d) 1 µm, e) 500 nm. Z-scale: a) 10 nm, b, c) 2°, d) 0.20 V, e) 0.10 V.

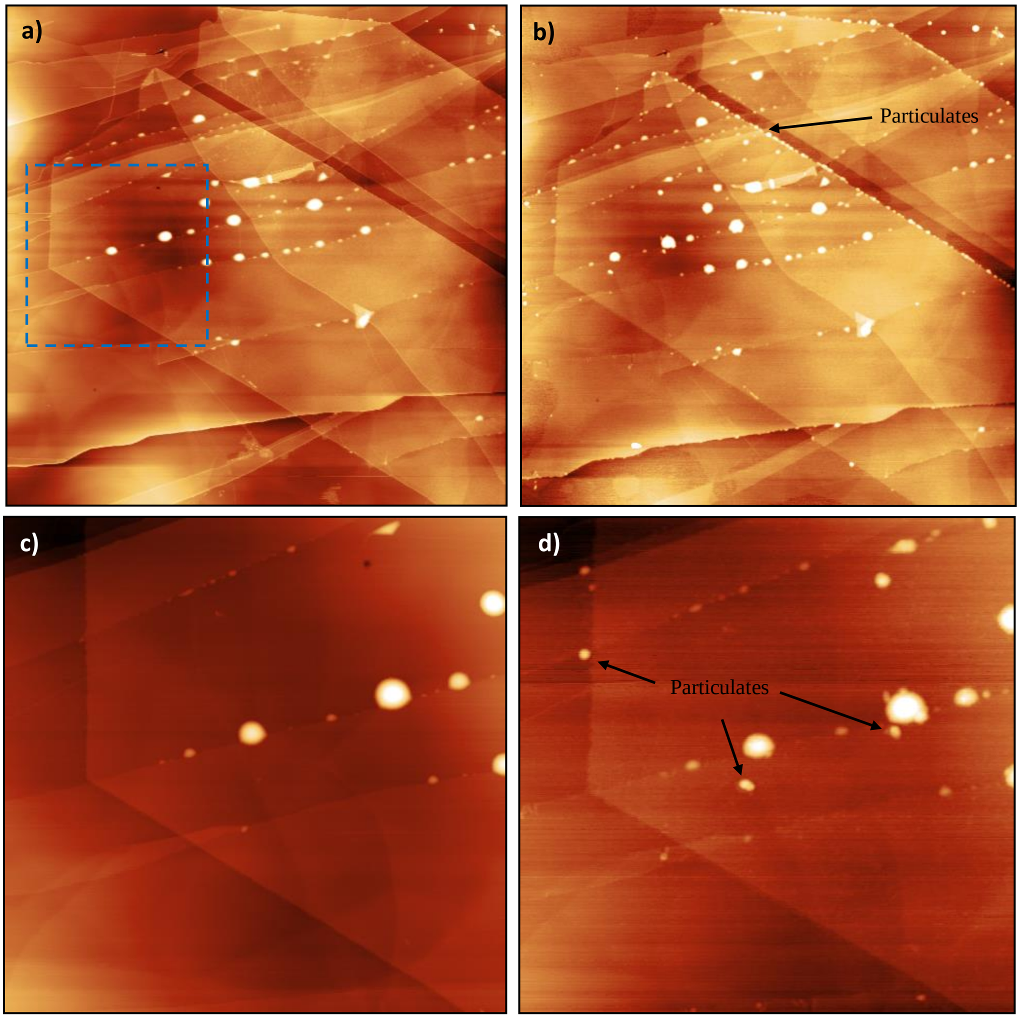

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Figure S6 - Particulate formation on MoS_2 Edges. a) AFM topograph of single-layer MoS_2 exfoliated on HOPG (42% RH and room temperature, same sample depicted in Figure S5). **b)** Topograph of same area as in a), taken approximately two weeks later. Particulates can be observed to have formed – primarily on the edges of the MoS_2 flake. **c)** Zoomed AFM topograph of approximate area indicated by blue square in a). **d)** Topograph of same area as in c), taken approximately two weeks later. Particulates dragged by the AFM tip are observed to catch on tears and defects on the surface, or on the sides of the water droplets. Topographs a) and b) depict the same area (approx. 5 µm x 5 µm), and topographs c) and d) represent the same area (approx. 2 µm x 2 µm). Z-scale: a, b) 10 nm, c, d) 15 nm.

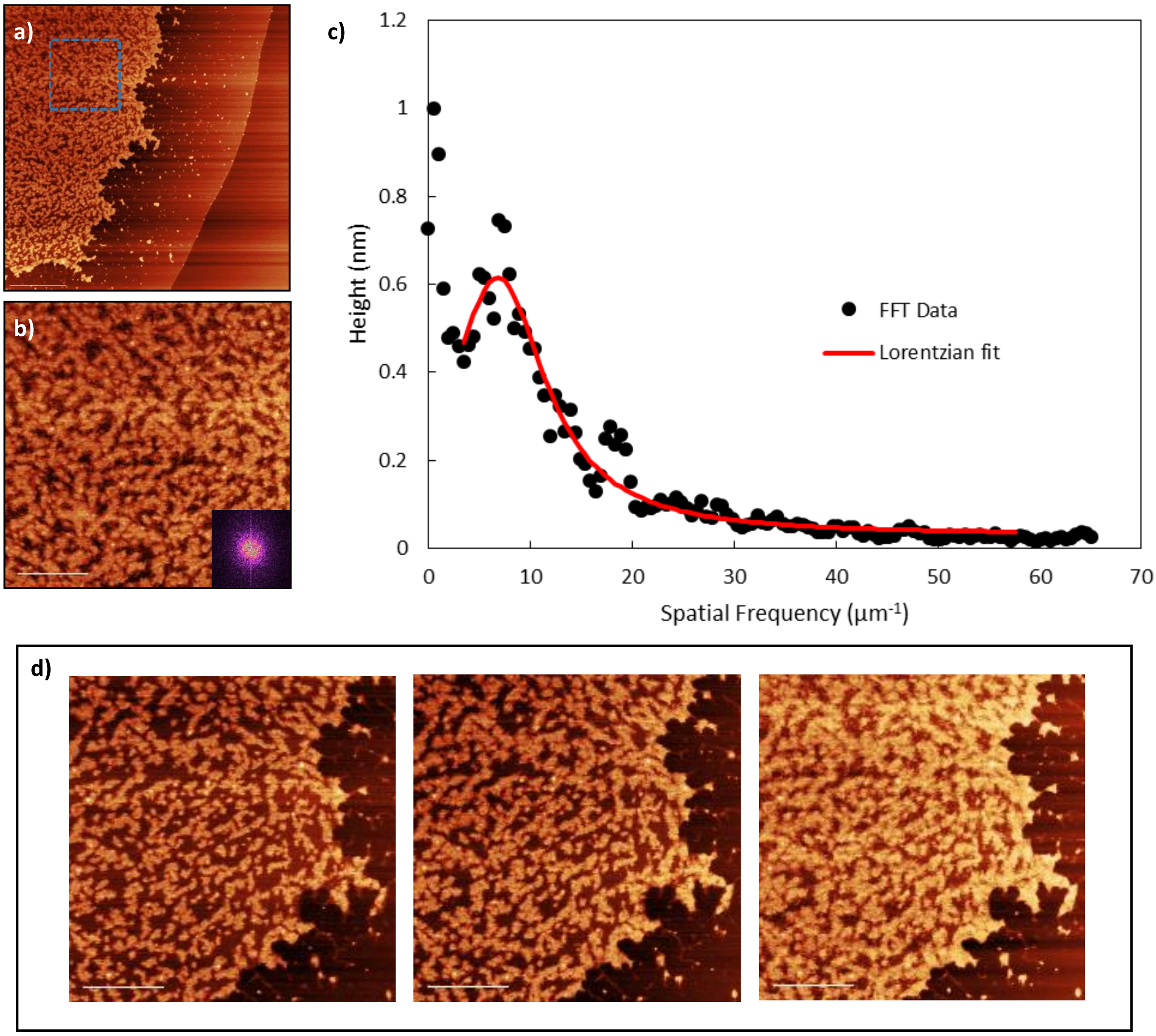

Figure S7 - Fourier Transform of D_2O Ice Clusters underneath Single-Layer MoS_2. a) AFM topograph of single-layer MoS_2-D_2O-mica system (same as in Figure 4b). **b)** Zoomed AFM topograph of area indicated by blue square in a). Inset: 2D FFT of b). **c)** Fourier Transform data show peak features of about 6-7 A° in height at a spatial frequency of approximately 7 μm^{-1}. Red curve represents Lorentzian fit to FFT data. **d)** Evolution of D_2O ice cluster structures over multiple scans (beginning from left to right), shown over a total period of approximately 90 min. (FT data are of sample at last stage shown in d). Lateral scale-bar: a) 1 µm, b, d) 500 nm. Z-scale: a) 10 nm, b) 3 nm, inset) 1.5 nm, d) 3 nm for all images.

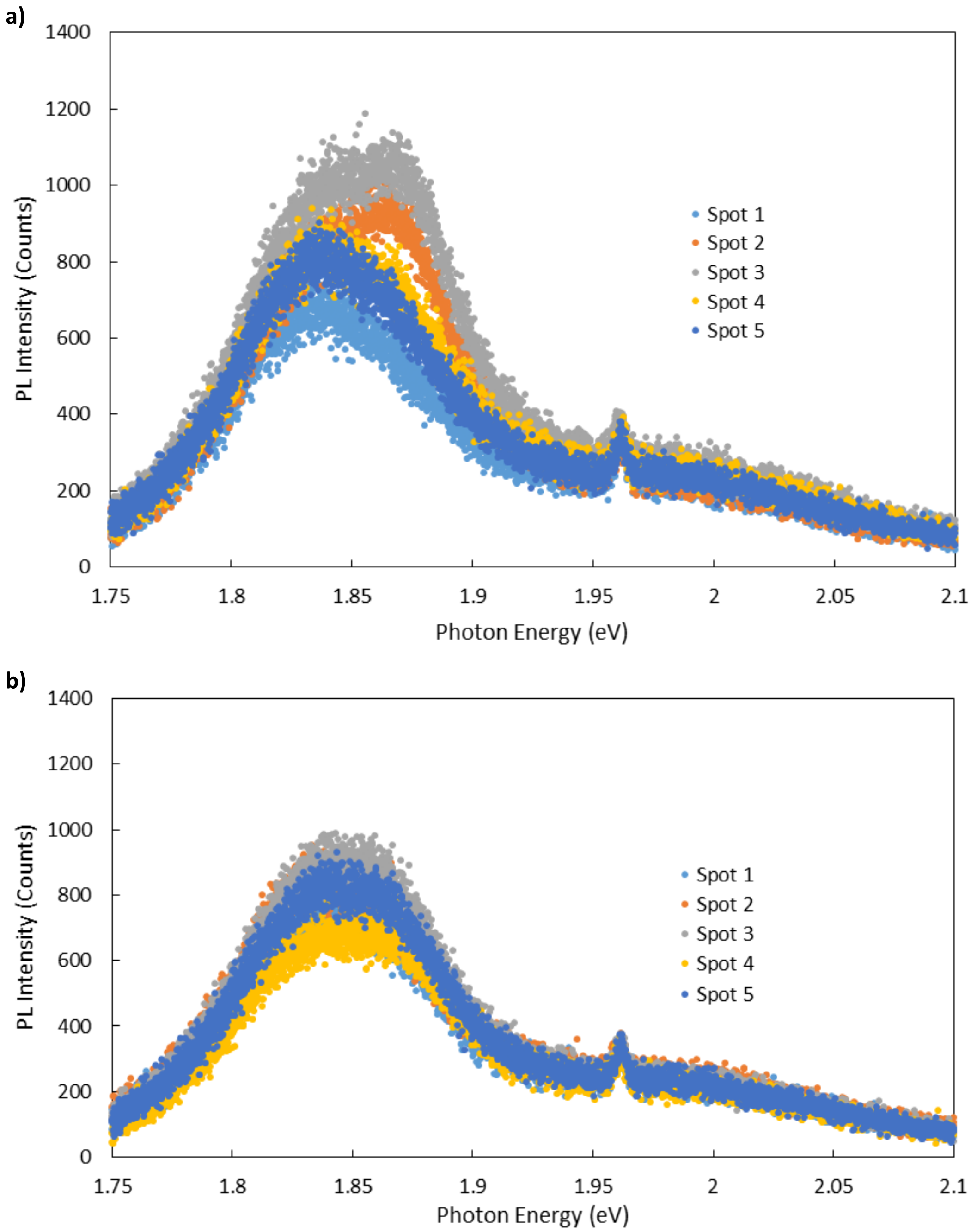

Figure S8 - Variations in H_2O-Quenched Spectra vs. D_2O-Quenched Spectra. a) Photoluminescence spectra of H_2O-covered areas of single-layer MoS_2. **b)** Photoluminescence spectra of D_2O-covered areas of single-layer MoS_2. PL spectra of D_2O-covered areas show less variation than spectra of H_2O-covered areas obtained at the same conditions. (Spectra represent 1 accumulation in both cases – fewer accumulations were used to limit possible variations due to longer exposure to the laser – differences between H_2O-quenched and D_2O-quenched spectra were still apparent. More accumulations improved signal-to-noise ratio but showed same trend).

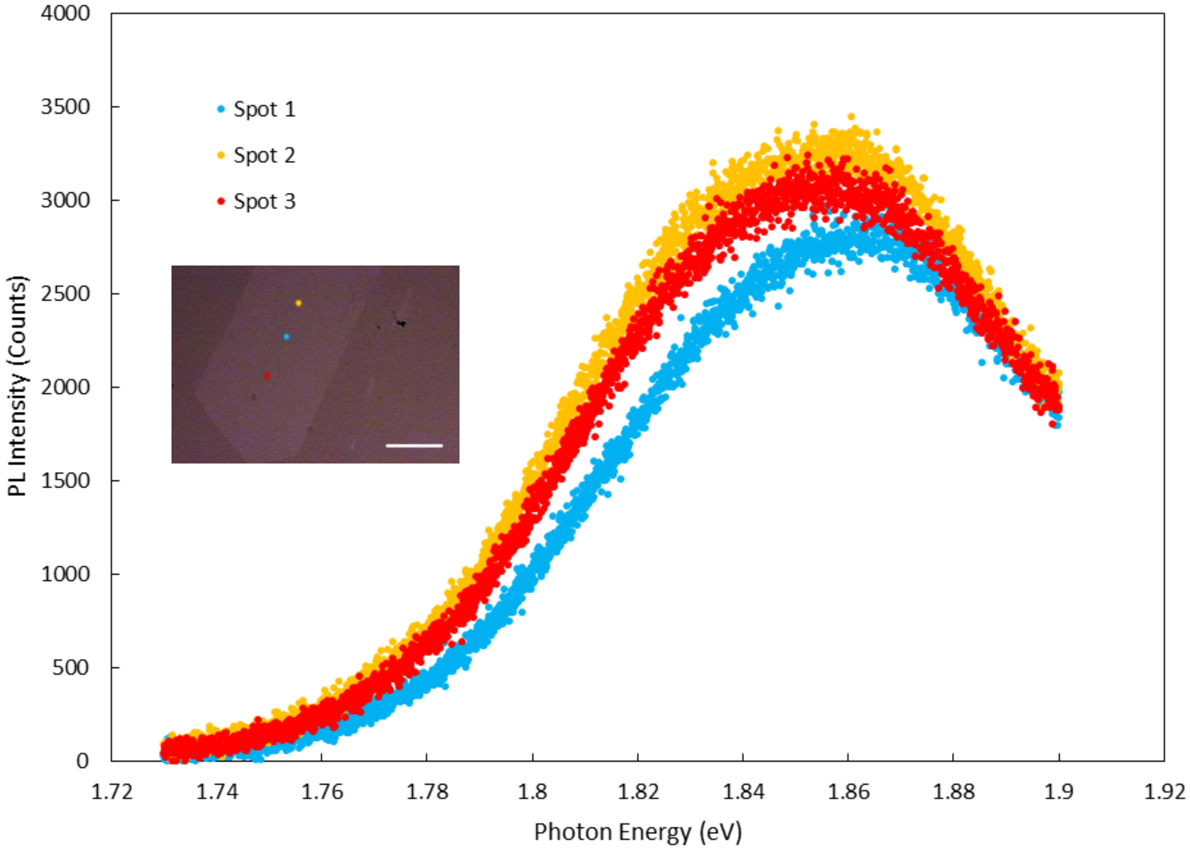

Figure S9 - Photoluminescence Spectra of Single-Layer MoS_2 on Mica. PL spectra of water-covered areas of single-layer MoS_2 on mica, showing little variation in lineshape or spectral position, acquired at a power density of 7 kW/cm^2. Inset: optical image of spots where spectra were acquired in corresponding colors. (Laser alignment crosshairs digitally removed for clarity). Lateral scale-bar: inset) 10 µm.

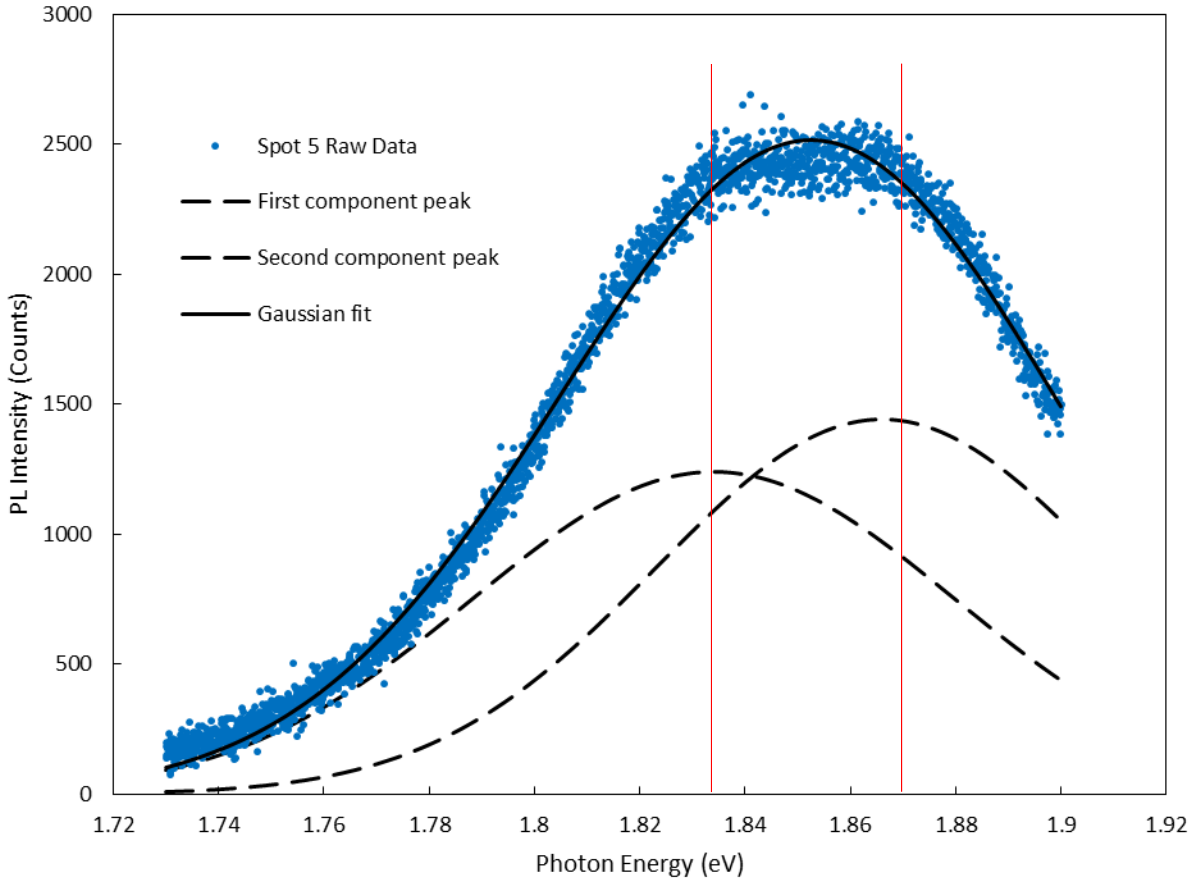

Figure S10 - Gaussian Fits of Quenched 2-Peak PL Spectra. Gaussian fit of spectrum depicted for spot 5 in Figure 3 of the main text is reproduced above as an example. Raw data are shown in blue, Gaussian fit as a solid black curve, and the two component peaks of the Gaussian fit as dashed black curves. The two peak features in the spectra occur at the spectral positions indicated by red vertical lines – at approximately 1.83 and 1.87 eV.

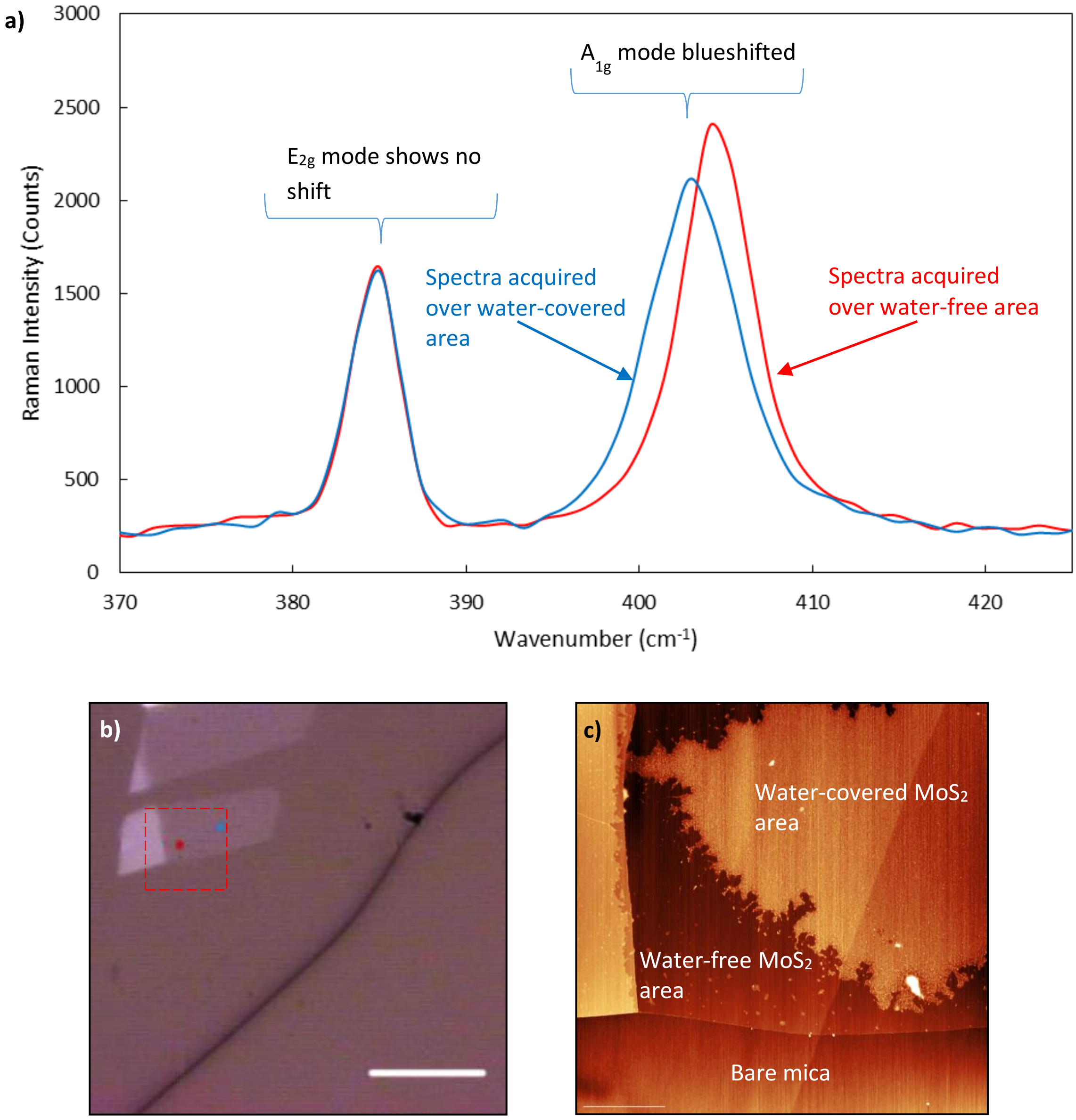

Figure S11 - Raman Spectra of Single-Layer MoS_2 on Mica. a) Raman spectrum of a representative single-layer MoS_2 sample shown with distinct peaks at about 385 and 405 cm^{-1} (red curve), in agreement with previous studies.[2,5] Raman spectra are shown for both single-layer molybdenum disulfide covering bare mica (red), and single-layer molybdenum disulfide resting on top of water sandwiched between the MoS_2 and mica surface (blue). A blueshift of 1 cm^{-1} was consistently observed for different samples in the A_{1g} mode at 405 cm^{-1} associated with out-of-plane vibrations of solely sulfur atoms. No shift was observed in the E_{2g} mode at 385 cm^{-1} associated with in-plane vibrations of sulfur atoms with respect to the molybdenum atom.[2,6] **b)** Optical image of spots on the sample where Raman spectra were acquired. Red spot taken over water-free area, blue spot taken over water-covered area. Dashed red box indicates approximate area corresponding to AFM image in c). (Laser alignment crosshairs digitally removed for clarity). **c)** AFM topograph of sample area used to acquire Raman data. Lateral scale-bar: b) 10 µm, c) 1 µm. Z-scale: c) 4 nm.

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